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(54) **METHODS OF PRODUCING PRE-LITHIATED SILICON OXIDE ELECTROACTIVE MATERIALS COMPRISING SILICIDES AND SILICATES**

(71) Applicant: **GM GLOBAL TECHNOLOGY OPERATIONS LLC**, Detroit, MI (US)

(72) Inventors: **Zhongyi Liu**, Troy, MI (US); **Xiaosong Huang**, Novi, MI (US); **Bradley R. Frieberg**, Farmington Hills, MI (US)

(73) Assignee: **GM GLOBAL TECHNOLOGY OPERATIONS LLC**, Detroit, MI (US)

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H01M 10/0525 (2010.01)

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CPC ***C01B 33/06*** (2013.01); ***C01B 33/32*** (2013.01); ***H01M 10/0525*** (2013.01)

(58) **Field of Classification Search**

CPC C01B 33/06; H01M 10/0525; Y02E 60/10
See application file for complete search history.

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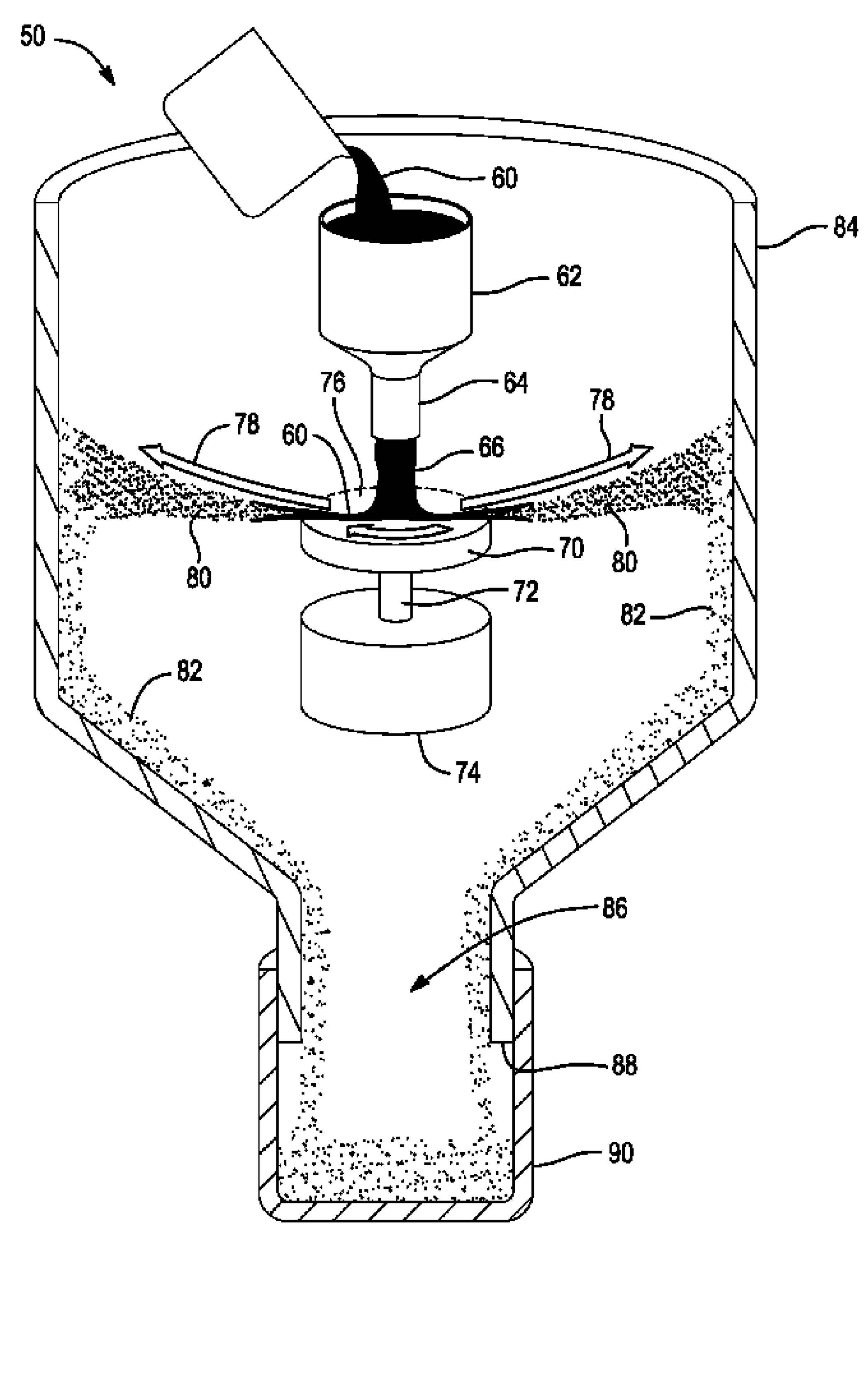
Primary Examiner — Anthony J Zimmer
Assistant Examiner — Jordan W Taylor
(74) *Attorney, Agent, or Firm* — Harness, Dickey & Pierce, P.L.C.

(57) **ABSTRACT**

Methods of making a negative electrode material for an electrochemical cell that cycles lithium ions is provided. The method may include centrifugally distributing a molten precursor comprising silicon, oxygen, and lithium by contacting the molten precursor with a rotating surface in a centrifugal atomizing reactor. The molten precursor is formed by combining lithium, silicon, and oxygen. For example, the precursor may be formed from a mixture comprising silicon dioxide (SiO_2), lithium oxide (Li_2O), and silicon (Si). The method may further include solidifying the molten precursor to form a plurality of substantially round solid electroactive particles comprising a mixture of lithium silicide (Li_ySi, where $0<y\leq4.4$) and a lithium silicate (Li_4SiO_4) and having a D50 diameter of less than or equal to about 20 micrometers.

19 Claims, 3 Drawing Sheets



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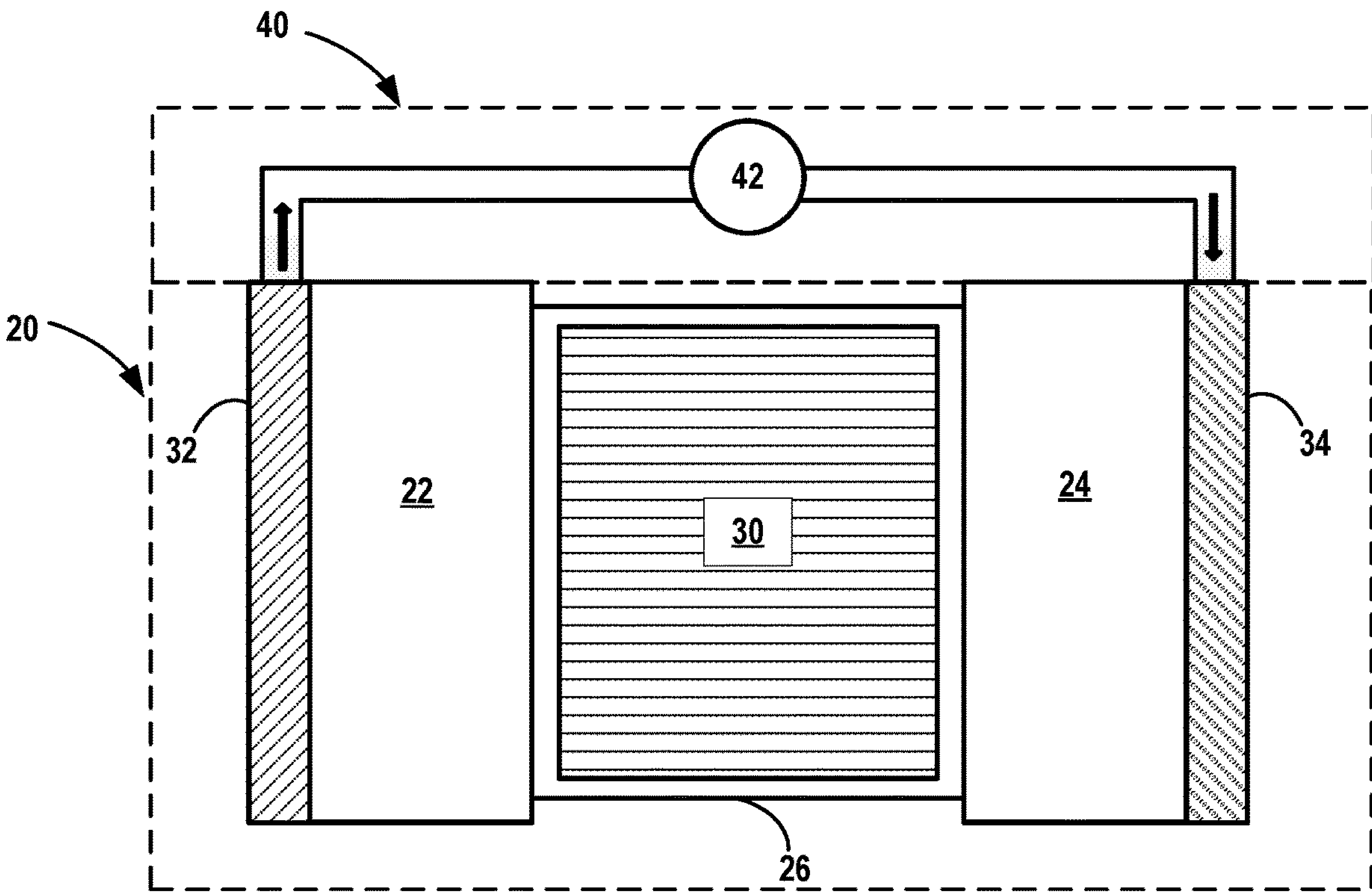

FIG. 1

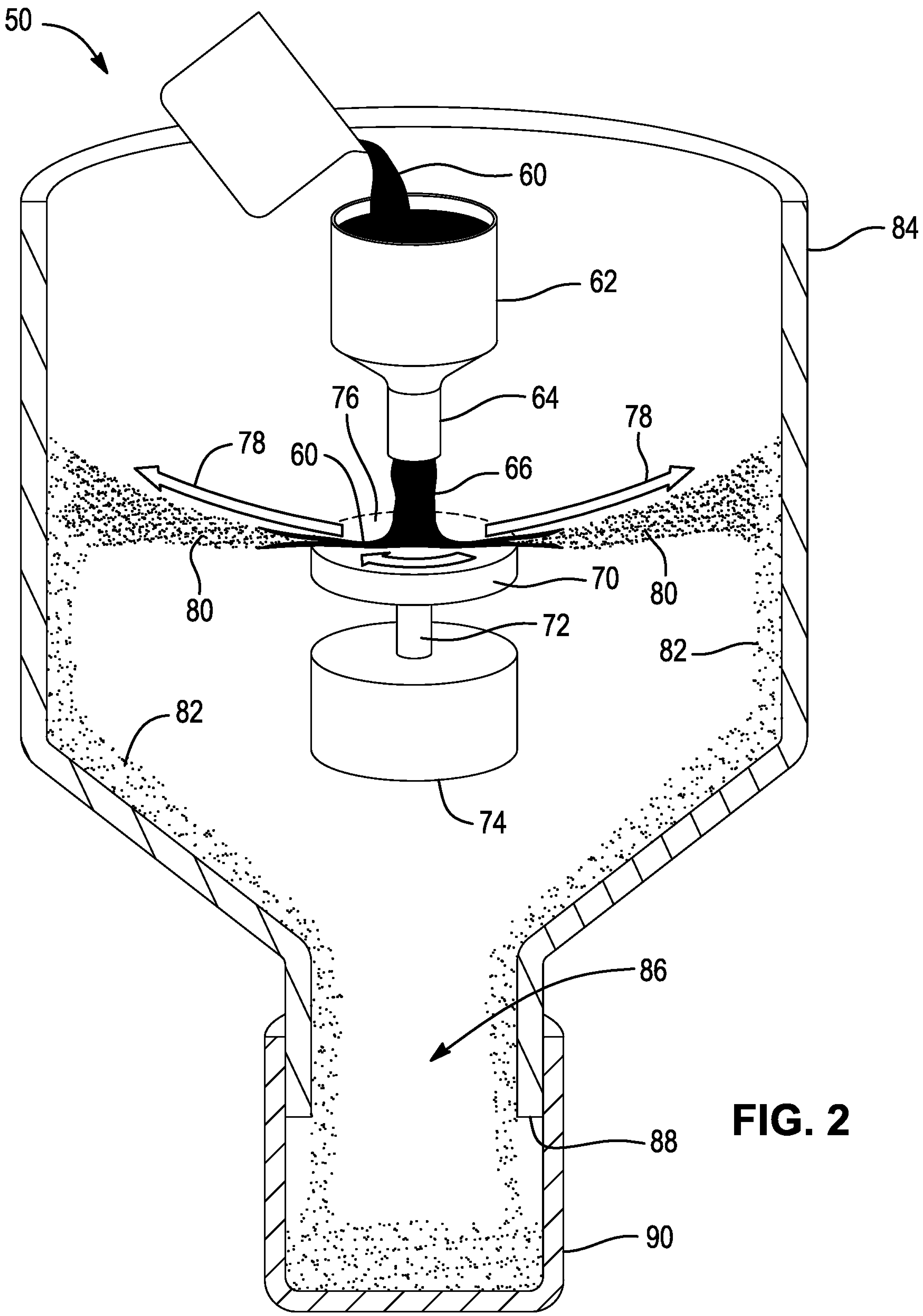

FIG. 2

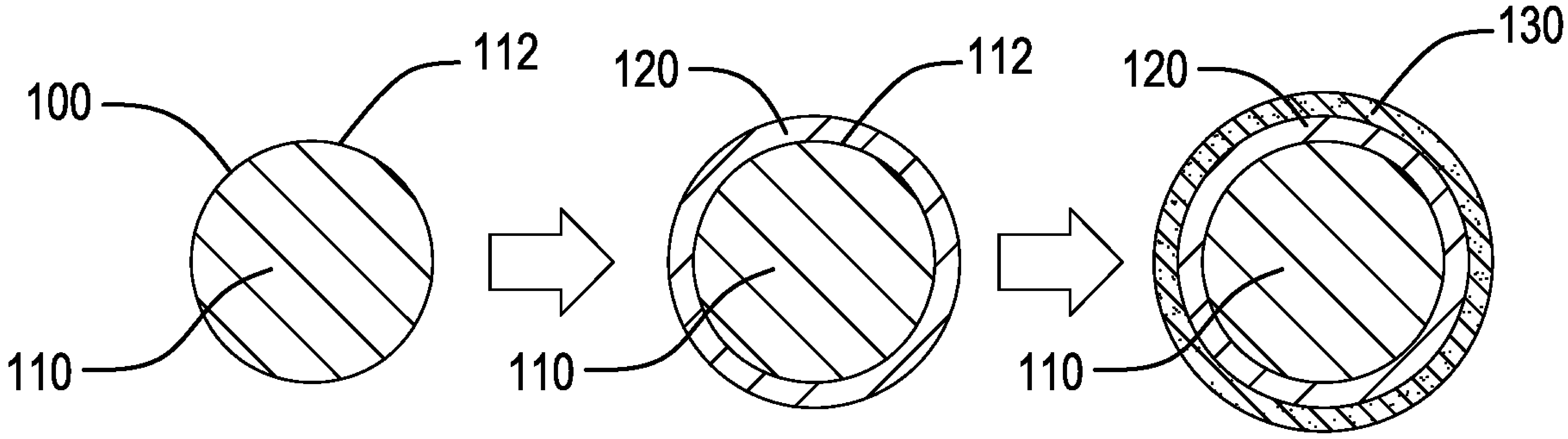

FIG. 3

METHODS OF PRODUCING PRE-LITHIATED SILICON OXIDE ELECTROACTIVE MATERIALS COMPRISING SILICIDES AND SILICATES

INTRODUCTION

This section provides background information related to the present disclosure which is not necessarily prior art.

The present disclosure pertains to methods of forming prelithiated electroactive materials for use in negative electrodes of lithium ion electrochemical cells. The method includes centrifugally distributing a molten precursor comprising silicon, lithium oxide, and optionally silicon oxide in a centrifugal atomizing reactor that forms a prelithiated silicon oxide material having a mixture of lithium silicide and lithium silicate.

Typical electrochemically active materials for forming anode of negative electrode materials for lithium ion electrochemical cells or batteries include lithium-graphite intercalation compounds, lithium-silicon alloying compounds, lithium-tin alloying compounds, and lithium alloys. While graphite compounds are most common, recently, anode materials with high specific capacity (in comparison with conventional graphite) are of growing interest. For example, silicon has the highest known theoretical charge capacity for lithium, making it one of the most promising materials for rechargeable lithium ion batteries. However, current anode materials comprising silicon can potentially suffer from significant drawbacks.

For example, during an initial lithiation and delithation cycle, the silicon-based electroactive material can undergo excessive volumetric expansion and contraction. Further, additional volumetric changes may occur during successive charging and discharging cycles is observed for silicon electroactive materials. Such volumetric changes can lead to fatigue cracking and decrepitation of the electroactive material. This may potentially lead to a loss of electrical contact between the silicon-containing electroactive material and the rest of the battery cell as well as the consumption of electrolyte to form new solid electrolyte interface (SEI), resulting in a decline of electrochemical cyclic performance, diminished Coulombic charge capacity retention (capacity fade), and limited cycle life. This is especially true at electrode loading levels required for the application of silicon containing electrodes in high-energy lithium ion batteries, such as those used in transportation applications.

While pre-lithiation of certain silicon based active materials prior to incorporation into the electrochemical cell has been used to minimize some of these shortcomings, pure lithium and other expensive reactants are often reactants used for prelithiation. Pure lithium is highly reactive and thus makes handling more complex during the manufacturing process. Accordingly, it would be desirable to develop methods of prelithiating electroactive materials comprising silicon that can employ more commonly available reactants and can avoid some of the handling restrictions that may be required for lithium, while enabling electroactive materials that are capable of minimal capacity fade and maximized charge capacity in commercial lithium ion batteries with long lifespans, especially for transportation applications.

SUMMARY

This section provides a general summary of the disclosure, and is not a comprehensive disclosure of its full scope or all of its features.

The present disclosure relates to methods of making a negative electrode material for an electrochemical cell that cycles lithium ions. In certain aspects, the method including centrifugally distributing a molten precursor including silicon, oxygen, and lithium by contacting the molten precursor with a rotating surface in a centrifugal atomizing reactor. The method also includes solidifying the molten precursor to form a plurality of substantially round solid electroactive particles including a mixture of lithium silicide (Li_ySi, where $0<y\leq4.4$) and a lithium silicate (Li_4SiO_4) and having a D50 diameter of less than or equal to about 20 micrometers.

In certain aspects, the molten precursor is formed by melting a precursor including silicon (Si) and lithium oxide (Li_2O).

In certain further aspects, the precursor includes a mole ratio of silicon (Si) to lithium oxide (Li_2O) of greater than or equal to about 1:2 to less than or equal to about 2:1.

In certain further aspects, the precursor further includes silicon dioxide (SiO_2).

In certain aspects, the lithium silicide is further represented by the formula $Li_{4.4x}Si$, where x is greater than 0 and less than or equal to about 0.85.

In certain aspects, the plurality of substantially round solid electroactive particles include a coating selected from the group consisting of: carbon-containing coatings, oxide-containing coatings, and combinations thereof.

In certain aspects, a temperature in the centrifugal atomizing reactor is greater than or equal to 400° C. to less than or equal to about 800° C. during the centrifugally distributing.

In certain aspects, an environment in the centrifugal atomizing reactor has less than or equal to about 0.5% by weight of any oxygen-bearing species.

In certain aspects, a flow rate of the centrifugal atomizing reactor is greater than or equal to 50 kg/hour to less than or equal to about 500 kg/hour.

In certain aspects, the D50 diameter is greater than or equal to about 1 μm to less than or equal to about 10 μm.

In certain aspects, the plurality of substantially round solid electroactive particles has a polydispersity index of less than or equal to about 1.2.

The present disclosure also further relates to a method of making a negative electrode material for an electrochemical cell that cycles lithium ions. The method includes centrifugally distributing a molten precursor by contacting the molten precursor with a rotating surface in a centrifugal atomizing reactor. The molten precursor is formed from a mixture including silicon dioxide (SiO_2), lithium oxide (Li_2O), and silicon (Si). The method includes solidifying the molten precursor to form a plurality of substantially round solid electroactive particles including a mixture of lithium silicide (Li_ySi, where $0<y\leq4.4$) and a lithium silicate (Li_4SiO_4) and having a D50 diameter of less than or equal to about 20 micrometers.

In certain aspects, the precursor includes a mole ratio of silicon (Si) to lithium oxide (Li_2O) of greater than or equal to about 1:2 to less than or equal to about 2:1.

In certain aspects, the lithium silicide is further represented by the formula $Li_{4.4x}Si$, where x is greater than 0 and less than or equal to about 0.85.

In certain aspects, a temperature in the centrifugal atomizing reactor is greater than or equal to 400° C. to less than or equal to about 800° C. during the centrifugally distributing.

In certain aspects, a flow rate of the centrifugal atomizing reactor is greater than or equal to 50 kg/hour to less than or equal to about 500 kg/hour.

In certain aspects, the D50 diameter is greater than or equal to about 1 μm to less than or equal to about 10 μm.

In certain aspects, the plurality of substantially round solid electroactive particles has a polydispersity index of less than or equal to about 1.2.

The present disclosure also further relates to a method of making a negative electrode material for an electrochemical cell that cycles lithium ions. The method includes melting a precursor mixture including lithium oxide (Li_2O) and silicon (Si) to form a molten precursor. The method also includes centrifugally distributing the molten precursor by contacting the molten precursor with a rotating surface in a centrifugal atomizing reactor. The method further includes solidifying the molten precursor to form a plurality of substantially round solid electroactive particles including lithium silicide (Li_ySi, where $0<y\leq4.4$) and a lithium silicate (Li_4SiO_4) and having a D50 diameter of less than or equal to about 20 micrometers.

In certain aspects, the precursor further includes silicon dioxide (SiO_2).

Further areas of applicability will become apparent from the description provided herein. The description and specific examples in this summary are intended for purposes of illustration only and are not intended to limit the scope of the present disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

The drawings described herein are for illustrative purposes only of selected embodiments and not all possible implementations, and are not intended to limit the scope of the present disclosure.

FIG. **1** is a schematic of an example electrochemical battery cell.

FIG. **2** shows an exemplary centrifugal atomizing reactor used in accordance with the present disclosure to form ultrafine solid electroactive material particles.

FIG. **3** is an illustration of a cross-sectional view of a negative electroactive material particle formed in accordance with certain aspects of the present disclosure, including a lithium-silicon-oxide composition forming a negative electroactive particle that can be treated to have a first coating and optionally further treated to have a second coating.

Corresponding reference numerals indicate corresponding parts throughout the several views of the drawings.

DETAILED DESCRIPTION

Example embodiments are provided so that this disclosure will be thorough, and will fully convey the scope to those who are skilled in the art. Numerous specific details are set forth such as examples of specific compositions, components, devices, and methods, to provide a thorough understanding of embodiments of the present disclosure. It will be apparent to those skilled in the art that specific details need not be employed, that example embodiments may be embodied in many different forms and that neither should be construed to limit the scope of the disclosure. In some example embodiments, well-known processes, well-known device structures, and well-known technologies are not described in detail.

The terminology used herein is for the purpose of describing particular example embodiments only and is not intended to be limiting. As used herein, the singular forms "a," "an," and "the" may be intended to include the plural forms as well, unless the context clearly indicates otherwise. The terms "comprises," "comprising," "including," and "having," are inclusive and therefore specify the presence of stated features, elements, compositions, steps, integers, operations, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components, and/or groups thereof. Although the open-ended term "comprising," is to be understood as a non-restrictive term used to describe and claim various embodiments set forth herein, in certain aspects, the term may alternatively be understood to instead be a more limiting and restrictive term, such as "consisting of" or "consisting essentially of." Thus, for any given embodiment reciting compositions, materials, components, elements, features, integers, operations, and/or process steps, the present disclosure also specifically includes embodiments consisting of, or consisting essentially of, such recited compositions, materials, components, elements, features, integers, operations, and/or process steps. In the case of "consisting of," the alternative embodiment excludes any additional compositions, materials, components, elements, features, integers, operations, and/or process steps, while in the case of "consisting essentially of," any additional compositions, materials, components, elements, features, integers, operations, and/or process steps that materially affect the basic and novel characteristics are excluded from such an embodiment, but any compositions, materials, components, elements, features, integers, operations, and/or process steps that do not materially affect the basic and novel characteristics can be included in the embodiment.

Any method steps, processes, and operations described herein are not to be construed as necessarily requiring their performance in the particular order discussed or illustrated, unless specifically identified as an order of performance. It is also to be understood that additional or alternative steps may be employed, unless otherwise indicated.

When a component, element, or layer is referred to as being "on," "engaged to," "connected to," or "coupled to" another element or layer, it may be directly on, engaged, connected or coupled to the other component, element, or layer, or intervening elements or layers may be present. In contrast, when an element is referred to as being "directly on," "directly engaged to," "directly connected to," or "directly coupled to" another element or layer, there may be no intervening elements or layers present. Other words used to describe the relationship between elements should be interpreted in a like fashion (e.g., "between" versus "directly between," "adjacent" versus "directly adjacent," etc.). As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items.

Although the terms first, second, third, etc. may be used herein to describe various steps, elements, components, regions, layers and/or sections, these steps, elements, components, regions, layers and/or sections should not be limited by these terms, unless otherwise indicated. These terms may be only used to distinguish one step, element, component, region, layer or section from another step, element, component, region, layer or section. Terms such as "first," "second," and other numerical terms when used herein do not imply a sequence or order unless clearly indicated by the context. Thus, a first step, element, component, region, layer or section discussed below could be termed a second step, element, component, region, layer or section without departing from the teachings of the example embodiments.

Spatially or temporally relative terms, such as "before," "after," "inner," "outer," "beneath," "below," "lower," "above," "upper," and the like, may be used herein for ease of description to describe one element or feature's relationship to another element(s) or feature(s) as illustrated in the figures. Spatially or temporally relative terms may be intended to encompass different orientations of the device or system in use or operation in addition to the orientation depicted in the figures.

Throughout this disclosure, the numerical values represent approximate measures or limits to ranges to encompass minor deviations from the given values and embodiments having about the value mentioned as well as those having exactly the value mentioned. Other than in the working examples provided at the end of the detailed description, all numerical values of parameters (e.g., of quantities or conditions) in this specification, including the appended claims, are to be understood as being modified in all instances by the term "about" whether or not "about" actually appears before the numerical value. "About" indicates that the stated numerical value allows some slight imprecision (with some approach to exactness in the value; approximately or reasonably close to the value; nearly). If the imprecision provided by "about" is not otherwise understood in the art with this ordinary meaning, then "about" as used herein indicates at least variations that may arise from ordinary methods of measuring and using such parameters. For example, "about" may comprise a variation of less than or equal to 5%, optionally less than or equal to 4%, optionally less than or equal to 3%, optionally less than or equal to 2%, optionally less than or equal to 1%, optionally less than or equal to 0.5%, and in certain aspects, optionally less than or equal to 0.1%.

In addition, disclosure of ranges includes disclosure of all values and further divided ranges within the entire range, including endpoints and sub-ranges given for the ranges.

As used herein, the terms "composition" and "material" are used interchangeably to refer broadly to a substance containing at least the preferred chemical constituents, elements, or compounds, but which may also comprise additional elements, compounds, or substances, including trace amounts of impurities, unless otherwise indicated.

Example embodiments will now be described more fully with reference to the accompanying drawings.

The present technology pertains to improved electroactive materials for electrochemical cells, especially lithium-ion batteries. In various instances, such cells are used in vehicle or automotive transportation applications (e.g., motorcycles, boats, tractors, buses, motorcycles, mobile homes, campers, and tanks). However, the present technology may be employed in a wide variety of other industries and applications, including aerospace components, consumer goods, devices, buildings (e.g., houses, offices, sheds, and warehouses), office equipment and furniture, and industrial equipment machinery, agricultural or farm equipment, or heavy machinery, by way of non-limiting example. In certain aspects, the lithium ion batteries can be used in a variety of consumer products and vehicles, such as Hybrid Electric Vehicles (HEVs) and Electric Vehicles (EVs).

An exemplary illustration of an electrochemical cell or battery for cycling lithium ions is shown in FIG. **1**. The battery **20** includes a negative electrode **22**, a positive electrode **24**, and a separator **26** (e.g., a microporous polymeric separator) disposed between the two electrodes **22**, **24**. The separator **26** comprises an electrolyte **30**, which may also be present in the negative electrode **22** and positive electrode **24**. A negative electrode current collector **32** may be positioned at or near the negative electrode, **22** and a positive electrode current collector **34** may be positioned at or near the positive electrode **24**. An interruptible external circuit **40** and load device **42** connects the negative electrode **22** (through its current collector **32**) and the positive electrode **24** (through its current collector **34**).

The battery **20** can generate an electric current during discharge by way of reversible electrochemical reactions that occur when the external circuit **40** is closed (to connect the negative electrode **22** and the positive electrode **24**) and the negative electrode **22** has a lower potential than the positive electrode. The chemical potential difference between the positive electrode **24** and the negative electrode **22** drives electrons produced by a reaction, for example, the oxidation of intercalated lithium, at the negative electrode **22** through the external circuit **40** towards the positive electrode **24**. Lithium ions that are also produced at the negative electrode **22** are concurrently transferred through the electrolyte **30** contained in the separator **26** towards the positive electrode **24**. The electrons flow through the external circuit **40** and the lithium ions migrate across the separator **26** containing the electrolyte solution **30** to form intercalated lithium at the positive electrode **24**. As noted above, electrolyte **30** is typically also present in the negative electrode **22** and positive electrode **24**. The electric current passing through the external circuit **40** can be harnessed and directed through the load device **42** until the lithium in the negative electrode **22** is depleted and the capacity of the battery **20** is diminished.

The battery **20** can be charged or re-energized at any time by connecting an external power source to the lithium ion battery **20** to reverse the electrochemical reactions that occur during battery discharge. Connecting an external electrical energy source to the battery **20** promotes a reaction, for example, non-spontaneous oxidation of intercalated lithium, at the positive electrode **24** so that electrons and lithium ions are produced. The lithium ions flow back towards the negative electrode **22** through the electrolyte **30** across the separator **26** to replenish the negative electrode **22** with lithium (e.g., intercalated lithium) for use during the next battery discharge event. As such, a complete discharging event followed by a complete charging event is considered to be a cycle, where lithium ions are cycled between the positive electrode **24** and the negative electrode **22**. The external power source that may be used to charge the battery **20** may vary depending on the size, construction, and particular end-use of the battery **20**. Some notable and exemplary external power sources include, but are not limited to, an AC-DC converter connected to an AC electrical power grid though a wall outlet and a motor vehicle alternator.

In many lithium-ion battery configurations, each of the negative electrode current collector **32**, negative electrode **22**, the separator **26**, positive electrode **24**, and positive electrode current collector **34** are prepared as relatively thin layers (for example, from several microns to a fraction of a millimeter or less in thickness) and assembled in layers connected in electrical parallel arrangement to provide a suitable electrical energy and power package. The negative electrode current collector **32** and positive electrode current collector **34** respectively collect and move free electrons to and from an external circuit **40**.

Further, the separator **26** operates as an electrical insulator by being sandwiched between the negative electrode **22** and the positive electrode **24** to prevent physical contact and thus, the occurrence of a short circuit. The separator **26** provides not only a physical and electrical barrier between the two electrodes **22**, **24**, but also contains the electrolyte solution in a network of open pores during the cycling of lithium ions, to facilitate functioning of the battery **20**.

Furthermore, the battery **20** can include a variety of other components that while not depicted here are nonetheless known to those of skill in the art. For instance, the battery **20** may include a casing, gaskets, terminal caps, tabs, battery terminals, and any other conventional components or materials that may be situated within the battery **20**, including between or around the negative electrode **22**, the positive electrode **24**, and/or the separator **26**. The battery **20** described above includes a liquid electrolyte and shows representative concepts of battery operation. However, the battery **20** may also be a solid-state battery that includes a solid-state electrolyte that may have a different design, as known to those of skill in the art.

As noted above, the size and shape of the battery **20** may vary depending on the particular application for which it is designed. Battery-powered vehicles and hand-held consumer electronic devices, for example, are two examples where the battery **20** would most likely be designed to different size, capacity, and power-output specifications. The battery **20** may also be connected in series or parallel with other similar lithium-ion cells or batteries to produce a greater voltage output, energy, and power if it is required by the load device **42**. Accordingly, the battery **20** can generate electric current to a load device **42** that is part of the external circuit **40**. The load device **42** may be powered by the electric current passing through the external circuit **40** when the battery **20** is discharging. While the electrical load device **42** may be any number of known electrically-powered devices, a few specific examples include an electric motor for an electrified vehicle, a laptop computer, a tablet computer, a cellular phone, and cordless power tools or appliances. The load device **42** may also be an electricity-generating apparatus that charges the battery **20** for purposes of storing electrical energy.

With renewed reference to FIG. **1**, the positive electrode **24**, the negative electrode **22**, and the separator **26** may each include an electrolyte solution or system **30** inside their pores, capable of conducting lithium ions between the negative electrode **22** and the positive electrode **24**. Any appropriate electrolyte **30**, whether in solid, liquid, or gel form, capable of conducting lithium ions between the negative electrode **22** and the positive electrode **24** may be used in the lithium-ion battery **20**. In certain aspects, the electrolyte **30** may be a non-aqueous liquid electrolyte solution that includes a lithium salt dissolved in an organic solvent or a mixture of organic solvents. Numerous conventional non-aqueous liquid electrolyte **30** solutions may be employed in the lithium-ion battery **20**.

In certain aspects, the electrolyte **30** may be a non-aqueous liquid electrolyte solution that includes one or more lithium salts dissolved in an organic solvent or a mixture of organic solvents. Numerous aprotic non-aqueous liquid electrolyte solutions may be employed in the lithium-ion battery **20**. For example, a non-limiting list of lithium salts that may be dissolved in an organic solvent to form the non-aqueous liquid electrolyte solution include lithium hexafluorophosphate ($LiPF_6$), lithium perchlorate ($LiClO_4$), lithium tetrachloroaluminate ($LiAlCl_4$), lithium iodide (LiI), lithium bromide (LiBr), lithium thiocyanate (LiSCN), lithium tetrafluoroborate ($LiBF_4$), lithium tetraphenylborate ($LiB(C_6H_5)_4$), lithium bis(oxalato)borate ($LiB(C_2O_4)_2$) (LiBOB), lithium difluorooxalatoborate ($LiBF_2(C_2O_4)$), lithium hexafluoroarsenate ($LiAsF_6$), lithium trifluoromethanesulfonate ($LiCF_3SO_3$), lithium bis(trifluoromethane) sulfonylimide ($LiN(CF_3SO_2)_2$), lithium bis(fluorosulfonyl) imide ($LiN(FSO_2)_2$) (LiSFI), and combinations thereof.

These and other similar lithium salts may be dissolved in a variety of aprotic organic solvents, including but not limited to, various alkyl carbonates, such as cyclic carbonates (e.g., ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC), fluoroethylene carbonate (FEC)), linear carbonates (e.g., dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylmethylcarbonate (EMC)), aliphatic carboxylic esters (e.g., methyl formate, methyl acetate, methyl propionate), γ-lactones (e.g., γ-butyrolactone, γ-valerolactone), chain structure ethers (e.g., 1,2-dimethoxyethane, 1-2-diethoxyethane, ethoxymethoxyethane), cyclic ethers (e.g., tetrahydrofuran, 2-methyltetrahydrofuran), 1,3-dioxolane), sulfur compounds (e.g., sulfolane), and combinations thereof.

The porous separator **26** may include, in certain instances, a microporous polymeric separator including a polyolefin. The polyolefin may be a homopolymer (derived from a single monomer constituent) or a heteropolymer (derived from more than one monomer constituent), which may be either linear or branched. If a heteropolymer is derived from two monomer constituents, the polyolefin may assume any copolymer chain arrangement, including those of a block copolymer or a random copolymer. Similarly, if the polyolefin is a heteropolymer derived from more than two monomer constituents, it may likewise be a block copolymer or a random copolymer. In certain aspects, the polyolefin may be polyethylene (PE), polypropylene (PP), or a blend of PE and PP, or multi-layered structured porous films of PE and/or PP. Commercially available polyolefin porous separator membranes **26** include CELGARD® 2500 (a monolayer polypropylene separator) and CELGARD® 2320 (a trilayer polypropylene/polyethylene/polypropylene separator) available from Celgard LLC.

In certain aspects, the separator **26** may further include one or more of a ceramic coating layer and a heat-resistant material coating. The ceramic coating layer and/or the heat-resistant material coating may be disposed on one or more sides of the separator **26**. The material forming the ceramic layer may be selected from the group consisting of: alumina (Al_2O_3), silica (SiO_2), and combinations thereof. The heat-resistant material may be selected from the group consisting of: Nomex, Aramid, and combinations thereof.

When the separator **26** is a microporous polymeric separator, it may be a single layer or a multi-layer laminate, which may be fabricated from either a dry or a wet process. For example, in certain instances, a single layer of the polyolefin may form the entire separator **26**. In other aspects, the separator **26** may be a fibrous membrane having an abundance of pores extending between the opposing surfaces and may have an average thickness of less than a millimeter, for example. As another example, however, multiple discrete layers of similar or dissimilar polyolefins may be assembled to form the microporous polymer separator **26**. The separator **26** may also comprise other polymers in addition to the polyolefin such as, but not limited to, polyethylene terephthalate (PET), polyvinylidene fluoride (PVdF), a polyamide, polyimide, poly(amide-imide) copolymer, polyetherimide, and/or cellulose, or any other material suitable for creating the required porous structure. The polyolefin layer, and any other optional polymer layers, may further be included in the separator **26** as a fibrous layer to help provide the separator **26** with appropriate structural and porosity characteristics. In certain aspects, the separator **26** may also be mixed with a ceramic material or its surface may be coated in a ceramic material. For example, a ceramic coating may include alumina (Al_2O_3), silicon dioxide (SiO_2), titania (TiO_2) or combinations thereof. Various conventionally available polymers and commercial products for forming the separator **26** are contemplated, as well as the many manufacturing methods that may be employed to produce such a microporous polymer separator **26**.

In various aspects, the porous separator **26** and the electrolyte **30** may be replaced with a solid-state electrolyte (SSE) (not shown) that functions as both an electrolyte and a separator. The SSE may be disposed between the positive electrode **24** and negative electrode **22**. The SSE facilitates transfer of lithium ions, while mechanically separating and providing electrical insulation between the negative and positive electrodes **22**, **24**. By way of non-limiting example, SSEs may include $LiTi_2(PO_4)_3$, $LiGe_2(PO_4)_3$, $Li_7La_3Zr_2O_{12}$, $Li_3xLa_{2/3}$-$xTiO_3$, Li_3PO_4, Li_3N, Li_4GeS_4, $Li_{10}GeP_2S_{12}$, Li_2S—P_2S_5, Li_6PS_5Cl, Li_6PS_5Br, Li_6PS_5I, Li_3OCl, $Li_{2.99}$ $Ba_{0.005}ClO$, or combinations thereof.

The positive electrode **24** may be formed from a lithium-based active material that can sufficiently undergo lithium intercalation and deintercalation, or alloying and dealloying, while functioning as the positive terminal of the battery **20**. One exemplary common class of known materials that can be used to form the positive electrode **24** is layered lithium transitional metal oxides. For example, in certain aspects, the positive electrode **24** may comprise one or more materials having a spinel structure, such as lithium manganese oxide ($Li_{(1+x)}Mn_2O_4$, where $0.1 \leq x \leq 1$),-lithium manganese nickel oxide ($LiMn_{(2-x)}Ni_xO_4$, where $0 \leq x \leq 0.5$) (e.g., $LiMn_{1.5}Ni_{0.5}O_4$); one or more materials with a layered structure, such as lithium cobalt oxide ($LiCoO_2$), lithium nickel manganese cobalt oxide ($Li(Ni_xMn_yCo_z)O_2$, where $0 \leq x \leq 1$, $0 \leq y \leq 1$, $0 \leq z \leq 1$, and $x+y+z=1$) (e.g., $LiMn_{0.33}Ni_{0.33}Co_{0.33}O2$), or a lithium nickel cobalt metal oxide ($LiNi_{(1-x-y)}Co_xM_yO_2$, where $0<x<0.2$, $y<0.2$, and M may be Al, Mg, Ti, or the like); or a lithium iron polyanion oxide with olivine structure, such as lithium iron phosphate ($LiFePO_4$), lithium manganese-iron phosphate ($LiMn_{2-x}Fe_xPO_4$, where $0<x<0.3$), or lithium iron fluorophosphate (Li_2FePO_4F).

In certain variations, the positive electroactive materials may be intermingled with an electronically conducting material that provides an electron conduction path and/or at least one polymeric binder material that improves the structural integrity of the electrode. For example, the electroactive materials and electronically or electrically conducting materials may be slurry cast with such binders, like polyvinylidene difluoride (PVdF), polytetrafluoroethylene (PTFE), ethylene propylene diene monomer (EPDM) rubber, or carboxymethyl cellulose (CMC), a nitrile butadiene rubber (NBR), styrene-butadiene rubber (SBR), lithium polyacrylate (LiPAA), sodium polyacrylate (NaPAA), sodium alginate, lithium alginate. Electrically conducting materials may include carbon-based materials, powdered nickel or other metal particles, or a conductive polymer. Carbon-based materials may include, for example, particles of graphite, acetylene black (such as KETCHEN™ black or DENKA™ black), carbon fibers and nanotubes, graphene, and the like. Examples of a conductive polymer include polyaniline, polythiophene, polyacetylene, polypyrrole, and the like. In certain aspects, mixtures of the conductive materials may be used. The positive electrode current collector **34** may be formed from aluminum (Al) or any other appropriate electrically conductive material known to those of skill in the art.

The negative electrode **22** includes an electroactive material as a lithium host material capable of functioning as a negative terminal of a lithium ion battery. The negative electrode current collector **32** may comprise a metal comprising copper, nickel, or alloys thereof or other appropriate electrically conductive materials known to those of skill in the art. In certain aspects, the positive electrode current collector **34** and/or negative electrode current collector **32** may be in the form of a foil, slit mesh, and/or woven mesh.

In certain aspects, the present disclosure provides methods of making negative electrodes **22** (e.g., anodes) that incorporate improved electrochemically active negative electrode materials. As discussed above, the negative electroactive materials suffer from significant volumetric expansion during lithium cycling (e.g., capable of accepting the insertion of lithium ions during charging of the electrochemical cell via lithiation or "intercalation" and releasing lithium ions during discharging of the electrochemical cell via delithiation or "deintercalation" or lithium alloying/dealloying). Such an electrochemically active negative electrode material may be selected from the group consisting of: silicon, silicon-containing alloys, graphite, and combinations thereof. By way of example, electroactive material particles comprising silicon may include silicon, or silicon containing binary and ternary alloys. In accordance with various aspects of the present teachings, a negative electroactive material can be incorporated into a negative electrode in an electrochemical cell.

Furthermore, in a typical manufacturing process, a negative electrode material is incorporated into the electrochemical cell without any lithium. The positive electrode has lithium and after cycling the electrochemical cell, lithium passes into and lithiates the negative electrode. However, in negative electroactive materials including silicon, for example, a portion of the lithium may not cycle back through the electrolyte to the positive electrode, but instead may remain with the negative electrode following the first lithiation cycle. This may be due to for example, formation of lithium silicates, such as Li_4SiO_4 and/or a solid electrolyte interphase (SEI) layer on the negative electrode, as well as ongoing lithium loss due to continuous solid electrolyte interphase (SEI) breakage. The solid electrolyte interface (SEI) layer can form over the surface of the negative electrode (anode), which is often generated by reaction products of anode material, electrolyte reduction, and/or lithium ion reduction. Such permanent loss of lithium ions may result in a decreased specific energy and power in the battery resulting from added positive electrode mass that does not participate in the reversible operation of the battery. For example, the lithium-ion battery may experience an irreversible capacity loss of greater than or equal to about 5% to less than or equal to about 30% after the first cycle.

Lithiation, for example pre-lithiation of the electroactive materials prior to incorporation into an electrochemical cell, may compensate for such lithium losses during cycling. Common lithiation methods, such as electrochemical, direct contact, and lamination methods; however, often require half-cell fabrication and teardown and/or high temperature chemical processes. Furthermore, it can be difficult to control an extent of lithiation that occurs during these processes. Further, these processes involve highly reactive chemicals and require additional manufacturing steps. These may be time consuming and potentially expensive processes. Further, such processes also commonly produce unworkable materials, for example anodes having undesirable thicknesses.

The present disclosure provides improved electroactive and electrode materials, and methods of making the same, which can address these challenges. In various aspects, the present disclosure provides advantages, including reducing mechanical stress in negative electrodes by forming pre-lithiated negative electroactive materials comprising silicon prior to forming the electrode. Notably, the electroactive materials are both formed and pre-lithiated in a single process. Further, the active lithium loss during formation cycles can be significantly reduced by the present technology. Additionally, cycle life performance of lithium ion batteries incorporating negative electrodes with negative electroactive materials comprising pre-lithiated silicon is improved in accordance with certain aspects of the present disclosure.

Prelithiation of reactant materials via centrifugal atomization can be conducted by lithiation of silicon by a reaction expressed by: $4.4xLi+Si \rightarrow Li_{4.4x}Si$, where $0<x\leq 1$. This prelithiation process may use relatively pure lithium (Li) metal and silicon (Si) as reactants. However, lithium metal is highly reactive and requires special handling and safety precautions. Moreover, while the product of such a reaction is lithium silicide ($Li_{4.4x}Si$, where $0<x\leq 1$) that is an electroactive material that is prelithiated, it still may undergo significant volumetric expansion during lithium cycling that occurs within battery operation.

Thus, in accordance with certain aspects of the present disclosure, methods are provided for making an electroactive material for a negative electrode of an electrochemical cell that cycles lithium ions, as described above. The method may be a process for creating pre-lithiated electroactive material particles, like lithiated silicon oxide alloys. The precursors for forming the lithiated silicon-containing electroactive materials include lithium, silicon, and oxygen. In certain variations, the precursor may be formed by combining lithium oxide (Li_2O) and silicon (Si). In certain other variations, the precursor may be formed by combining lithium oxide (Li_2O), silicon (Si), and optionally silicon dioxide or silica (SiO_2). These starting materials are more widely available and thus less expensive than pure lithium (Li) metal. Further, the manufacturing process requires fewer safety precautions in avoiding handling of pure lithium metal as a reactant, which is highly reactive.

Generally, production of lithium silicide (Li_ySi) and lithium silicate (Li_4SiO_4) may occur by a thermochemical reduction that involves the following reactions in Equations (1)-(3):

$$2Li_2O+Si=4Li+SiO_2 \tag{1}$$

$$yLi+Si=Li_ySi\text{(silicide), where } 0<y\leq 4.4 \tag{2}$$

$$2Li_2O+SiO_2=Li_4SiO_4\text{(silicate)} \tag{3}$$

The heat of formation of Li_2O is about (−600 kJ/mol) and SiO_2 (−910 KJ/mol).

Thus, starting from Li_2O, Si, and/or SiO_2 reactant materials, a thermochemical reaction is conducted that forms prelithiated silicon oxide (SiO_x) particles that comprise both electroactive lithium silicides (e.g., Li_ySi, where $0<y\leq 4.4$, for example, in certain variations, $Li_{4.4x}Si$, where $0<x\leq$about 0.85) and inactive lithium silicates. Lithium silicates may include Li_4SiO_4, Li_8SiO_6, Li_2SiO_3, and $Li_2Si_2O_5$. In certain aspects, the lithium silicate(s) formed in the thermochemical reaction may be represented by Li_4SiO_4, which is believed to be the dominant and most stable lithium silicate (having highest melting point), although as appreciated by those of skill in the art may include other lithium silicates in the final product. Notably, as shown in Equation (4), for a silicon oxide (SiO) product that is lithiated, part of the lithiation reaction of silicon oxide is reversible (formation of the electroactive lithium silicide), while part of the situation reaction that occurs is irreversible (formation of the lithium silicate).

$$SiO+4Li \rightarrow 0.75Li_4Si\text{(reversible)}+0.25Li_4SiO_4\text{(irreversible)} \tag{4}$$

Thus, when silicon oxide based electroactive materials are incorporated into an electrochemical cell, lithium (Li) consumption may occur during cycling by formation of the lithium silicate (Li_4SiO_4) and/or formation of the SEI layer on a surface of the electroactive material. However, where the silicon oxide material is prelithiated in accordance with certain aspects of the present teachings, it reduces consumption of lithium during initial cycling of the cell by having already formed the irreversible lithium silicate product. Notably, the silicon-oxide containing product formed in accordance with certain aspects of the present disclosure may have a predetermined amount of electrochemically inert lithium silicate combined with electroactive lithium silicide.

However, the presence lithium silicate (mixed with the lithium silicide) in the electroactive material particles can provide certain advantages to the electroactive material, for example, enhancing mechanical strength and reducing volumetric expansion changes that may occur during lithiation and prelithiation to reduce stress on the electroactive materials during cycling and thus reduce the potential for cracking, decrepitation, and the like. Thus, the silicon-oxide containing products comprising both lithium silicide and lithium silicates are more robust than a comparable electroactive material that predominantly contains lithium silicide alone.

In certain aspects, a silicon oxide final product includes a lithium silicate, which may be represented by Li_4SiO_4 where a ratio of Li/Si is about 4 (e.g., 4:1), and a lithium silicide, $Li_{4.4y}Si$, where a ratio of Li/Si is greater than 0 to about 4.4. Thus, an overall ratio of Li/Si may range from greater than 0 to about 4.4. For a precursor including Li_2O and Si, a ratio of Li_2O/Si may range from greater than 0 to about 2.2. In certain non-limiting aspects, a mole ratio of the lithium oxide (Li_2O) to silicon (Si) in a precursor may be about 2:1 to about 1:2 (6 moles of excess Si) when using silicon (Si) to control the constituents of the final product. In alternative aspects, lithium oxide (Li_2O) and silicon oxide (SiO_2) may be used to control the constituents of the final product.

These pre-lithiated electroactive material particles may further have one or more coatings applied thereon, such as a carbonaceous coating and/or an oxide-based coating, described in U.S. Patent Publication No. 2021/0175491 entitled "Methods of Forming Prelithiated Silicon Alloy Electroactive Materials," the relevant portions of which are incorporated herein by reference. These oxide-based coatings may comprise aluminum oxide (Al_2O_3), titanium oxide coating (TiO_2), vanadium pentoxide coating (V_2O_5), zirconium oxide coating (ZrO_2), hafnium oxide (HfO_2), zinc oxide coating (ZnO), silicon oxide (SiO_2), and combinations thereof. The coating may comprise an electrically conductive and ionically conductive layer that comprises a carbon-containing or carbonaceous material. In certain aspects, the electrically conductive and ionically conductive layer may comprise an amorphous carbon that generally lacks any crystalline structure or ordering or graphitic carbon. As will be described herein, the process may be performed via centrifugal/gas atomization that forms prelithiated SiO_x particles having an advantageous substantially spherical shape with a narrow size distribution range. Further, compared to other pre-lithiation methods, centrifugal/gas atomization is a high production rate process that provides a means to precisely control pre-lithiation levels and the phases formed in the product. Thus, a unique spherical composite structure is created that can stabilize the prelithiated silicon oxides (SiO_x) product and attain desired mechanical and electrochemical performance when used as a battery anode material.

In various aspects, the present disclosure provides controllable phase ratios in the final product. For example, phase ratios are controllable via controlling the relative amounts of starting materials, such as ratios of lithium oxide (Li_2O) and silicon provided in silicon metal (Si) or silicon dioxide (SiO_2). The final product of prelithiated silicon oxides (SiO_x) include a first component of silicide (e.g., Li_ySi) and a second component of silicate (e.g., Li_4SiO_4). In certain aspects, a stoichiometric ratio of lithium silicides (e.g., Li_ySi, where $0<y\leq4.4$) and inactive lithium silicates (e.g., Li_4SiO_4) formed in the product may be about 1:1 to about 3:1.

Thus, the present disclosure contemplates improving battery cycle life performance. Further, the present disclosure mitigates potential safety concerns in the manufacturing process that would otherwise occur if lithium metal was employed as a reactant for prelithiation. Further, the manufacturing process helps reduce raw material costs.

The present disclosure contemplates a method of making lithiated silicon electroactive materials from precursors comprising silicon, oxygen, and lithium by a centrifugal/gas atomization process. In centrifugal atomization processing, a molten material is directed towards at least one rotating disc or cup, where melt drops form and fly away from the rotating disc or cup to solidify and form spherical particle silicon oxides. Thus, in certain aspects, a method of making a negative electrode material for an electrochemical cell that cycles lithium ions is provided. The method comprises centrifugally distributing a molten precursor comprising silicon, lithium, and oxygen by contacting the molten precursor with a rotating surface in a centrifugal atomizing reactor and solidifying the molten precursor to form a plurality of substantially round solid electroactive particles comprising an alloy of lithium and silicon and having a D50 diameter of less than or equal to about 20 micrometers. In certain variations, the centrifugal atomization process forms a plurality of particles having a relatively small particle size (e.g., ultrafine particles) with a smaller particle size distribution (e.g., monodisperse).

FIG. **2** shows an exemplary centrifugal atomizing reactor **50**. It should be noted that the reactor **50** is a simplified version and may contain various other equipment. One suitable multistage centrifugal atomizing reactor suitable for forming the plurality of electroactive particles is described in U.S. Patent Publication No. 2021/0138548 entitled "Article for Producing Ultra-Fine Powders and Method of Manufacture Thereof," the relevant portions of which are incorporated herein by reference. A molten precursor material **60** can be conveyed in batches or continuously from an upstream furnace and introduced to a distribution vessel or tundish **62**. The tundish **62** has at least one outlet port **64** with a suitable diameter to facilitate a quick discharge of the molten precursor material **60**. The number and the diameter of the outlet ports **64** may be adjusted to control particle size during and after atomization process, as appreciated by those of skill in the art. Further, the tundish **62** may rotate or have a source of pressure to enhance discharge via the outlet port **64**. A stream **66** of molten precursor material **60** is discharged from the outlet port **64**.

The stream **66** contacts a surface **76** of a rotating component **70** that may be in the form of a disc or cup. The rotating component **70** is in rotary communication with a shaft **72** and a motor **74**. Rotary motion is transmitted from the motor **74** via the shaft **72** to the rotating component **70**. The rotary motion of the rotating component **70** imparts a centrifugal force to the molten precursor material **60**, which causes it to distribute and comminute the precursor material in a centrifugal direction **78** in the reactor **50** outwards from the central axis defined by the shaft **72**. As shown, the molten precursor material **60** contacts the rotating surface **76** and as it passes in an outward direction creates droplets **80** that solidify to form a plurality of substantially round solid electroactive particles **82**. While not shown, ultrasonic or mechanical vibration may be applied to the rotating component **70** to facilitate comminution of the molten material as well as de-agglomeration of particles. The droplets **80** are thrust outward. The solid particles **82** are outwardly thrust towards a wall **84** of the reactor **50** and then fall into an outlet region **86** that includes an outlet **88**. The ultrafine solid particles **82** are transported by gravity to the outlet **88**. As shown, a collection vessel **90** is connected to the outlet **88** and collects the particles **82**; however, as will be described in detail below, the outlet **88** alternatively may be in fluid communication with additional reactor chambers.

The solidified particles formed by such a process may be relatively small (e.g., fine or ultrafine) and have a substantially round shape. "Substantially round-shaped" includes particles having low aspect ratios and with a morphology or shape including spherical, orbed, spheroidal, egg-shaped, elliptical, and the like. In certain variations, the particles have a spherical shape. Further, the solid particles may have an average diameter (D). A D50 means a cumulative 50% point of diameter (or 50% pass particle size) for the plurality of solid particles. In certain aspects, the D50 of the plurality of electroactive solid particles formed by a centrifugal atomization process is less than or equal to about 20 micrometers, optionally less than or equal to about 15 micrometers, optionally less than or equal to about 10 micrometers, and optionally less than or equal to about 5 micrometers. In certain variations, the D50 for the plurality of solid electroactive particles formed may be greater than or equal to about 1 μm to less than or equal to about 20 μm, optionally greater than or equal to about 1 μm to less than or equal to about 10 μm.

The plurality of electroactive solid particles formed by a centrifugal atomization process may be relatively monodisperse, for example, having a narrow polydispersity index or variation in particle sizes among the plurality of particles formed. In one aspect, the particle distribution is narrow having a polydispersity index of less than or equal to about 1.2, for example.

In certain aspects, the centrifugal atomization process of forming the plurality of electroactive materials may provide a high yield for the target or predetermined particle size diameter range. For example, where an average particle diameter is selected to be greater than or equal to about 1 μm to less than or equal to about 20 μm, an overall yield from the process for solid particles having the predetermined size range may be greater than or equal to about 10% to less than or equal to about 90%. These uniform diameter electroactive materials formed from an alloy of lithium and silicon may be used in various electrochemical cells/batteries and energy storage devices.

In certain variations, an environment in the centrifugal atomizing reactor may be substantially free of gaseous oxygen-containing species to avoid reaction with lithium. While lithium is not added as a precursor/reactant, it may form as an intermediate and thus as a precaution, the environment in which the reactions occur may be relatively inert. For example, the environment may have less than or equal to about 0.5% by weight of any oxygen-bearing species in a gas phase, for example, oxygen gas, water, and the like. The environment in the reactor optionally has a low water/moisture level reflected by a relative humidity (RH) of less than or 0.5% at reaction condition temperatures.

The centrifugal atomizing reactor may be capable of high throughput, for example, having a mass flow rate of greater than or equal to 50 kg/hour to less than or equal to about 500 kg/hour in forming the particles of electroactive materials with the desired range of average particle sizes. Higher flow rates may also be possible, so long as the particles formed have the desired D50. The flow rate has an effect on particle size. For example, the higher the flow rate of the molten material, the larger size of the particles that are produced. So the flow rate may be limited by the desired size of the particles.

Furthermore, the methods provided by certain aspects of the present disclosure advantageously provide a high level of control over the compositions of the electroactive materials formed. The methods of the present disclosure provide an ability to directly manufacture a pre-lithiated electroactive material comprising silicon, without the need for an initial formation step for the particle followed by a pre-lithiation step where lithium is introduced to the material. As noted above, the alloy comprising lithium and silicon that is formed by the present methods may be represented by the formula: lithium silicide (Li_ySi, where $0<y\leq4.4$) or in certain variations, $Li_{4.4x}Si$, where $0<x\leq$about 0.85. The precursor material for forming the electro active material alloy can be selected to have specific compositions that may form specific phases, depending on the temperature conditions selected during the centrifugal atomizing process in the reactor. Thus, precise control of the phases present in the particles formed can be attained through the composition of the melt.

In certain aspects, the precursor material has sufficient amounts of oxygen and lithium in combination with silicon to fully form the lithium silicate phase (Li_4SiO_4) phase. Additional amounts of lithium can be varied to form different variations of the Li—Si phase. As will be appreciated by those of skill in the art, it can be desirable to maximize a relative stoichiometric amount of lithium in the lithium-silicon alloy/electroactive material. In certain aspects, the precursor material is selected to have greater than 0 atomic % to less than or equal to about 82 at. % of lithium and correspondingly greater than or equal to about 18 atomic % to less than or equal to about 100 at. % of silicon, which generally corresponds to $Li_{4.4x}Si$, where x is greater than 0 to less than or equal to about 0.85. In other aspects, the precursor material optionally has greater than or equal to about 30 atomic % to less than or equal to about 70 at. % of lithium and correspondingly greater than or equal to about 30 atomic % to less than or equal to about 70 at. % of silicon, which generally corresponds to $Li_{4.4x}Si$, where x is greater than or equal to about 0.1 to less than or equal to about 0.5. In yet other aspects, the precursor material optionally has about 50 at. % of lithium and correspondingly greater than or equal to about 50 at. % of silicon, which generally corresponds to $Li_{4.4x}Si$, where x is about 0.25.

In certain aspects, the lithium silicide alloy formed after the centrifugal atomization process may comprise Li_ySi, where $0<y\leq4.4$) or in certain variations, $Li_{4.4x}Si$, where $0<x\leq$about 0.85. For example, the lithium silicide alloy formed after the centrifugal atomization process may comprise one or more of the following phases: $Li_{22}Si_5$, $Li_{13}Si_4$, Li_7Si_3, $Li_{12}Si_7$, and LiSi. Notably, in certain variations where a lower amount of lithium is present in the alloy, a phase comprising only Si may be present. In certain variations, the alloy may comprise one or more of the following phases: $Li_{22}Si_5$, $Li_{13}Si_4$, Li_7Si_3, $Li_{12}Si_7$, and LiSi. In addition to the lithium silicide alloy formed in the centrifugal atomization process, the silicon oxide product may also comprise lithium silicates including Li_4SiO_4, Li_8SiO_6, Li_2SiO_3, and/or $Li_2Si_2O_5$, by way of example.

In certain aspects, a temperature in the centrifugal atomizing reactor during centrifugal distribution of a molten precursor may be greater than or equal to 400° C. to less than or equal to about 1,000° C. Higher temperatures may be employed where the lithium, silicon, and oxygen precursors are miscible, to facilitate formation of the desired phases. In certain variations, a temperature in the centrifugal atomizing reactor during centrifugal distribution of a molten precursor may be greater than or equal to 400° C. to less than or equal to about 800° C. Compared to other pre-lithiation methods, centrifugal/gas atomization provided by certain aspects of the present disclosure provides a means to precisely control the extent of pre-lithiation and phases formed.

Thus, in various aspects, a centrifugal/gas atomizer reactor is used to produce particles that comprise pre-lithiated silicon alloys, including lithium silicide and lithium silicon oxides. Such a centrifugal/gas atomizer reactor provides high throughput production of lithium-silicon alloy electroactive particles having a relatively homogenous size distribution and thus, a high yield for a predetermined average particle size diameter. The presence of $Li_{4.4x}Si$ silicide alloy can reduce the lithium consumption and initial stress during formation cycles. This has the benefit of the electroactive material comprising silicon undergoing an initial volumetric expansion due to lithiation prior to being incorporated into an electrode to enhance the mechanical properties of the electrode that is initially formed. Conventionally, the electroactive material comprising silicon is incorporated into an electrode (e.g., mixed in with the polymeric matrix and other electrode components) and then lithiated where the initial expansion occurs. This expansion upon lithiation can cause mechanical stress and potential damage to not only the electroactive particles, but also the surrounding composite. For a conventional silicon electroactive material, the extent of volumetric expansion that occurs during an initial lithiation reaction can cause the silicon particle to mechanically degrade and break into a plurality of smaller fragments or pieces. When the particle breaks into smaller pieces, additional lithium is consumed to form new SEI and these fragments or smaller pieces can no longer maintain performance of the electrochemical cell. When electroactive materials are formed from the lithium and silicon alloys in accordance with the present disclosure, they have already undergone an initial volumetric expansion and thus incorporating them into an electrode only causes minimal expansion and contraction stress during lithium cycling.

Moreover, the presence of lithium silicate (Li_4SiO_4) further enhances the mechanical properties of the lithium silicon oxide product containing lithium silicide alloys. As noted above, it physically retains the lithium silicide(s) in a silicon oxide material and further reduces overall volumetric expansion and contraction during lithiation cycling.

Furthermore, the lithium-silicon alloy powder created by the centrifugal/gas atomization process can then be coated with one or more coatings to protect the underlying electroactive material and/or increase the electrical conductivity. Moreover, the lithium-silicon alloy particles can be exposed to a liquid electrolyte to form a surface solid electrolyte interface (SEI) layer before the electrode is fabricated.

An optional first coating is disposed over the surface of a negative electroactive material particle **100**, like that shown in FIG. **3**. In certain variations, a negative electroactive particle **100** having the core region **110** comprising the lithium silicide (Li_ySi, where $0<y\leq4.4$) and lithium silicate (Li_4SiO_4) and a first coating **120** may be incorporated into a negative electrode. However, in certain other variations, a multilayered coating may be formed over the negative electroactive particle **100**. Thus, a second coating **130** may be disposed over the first coating **120** and the core region **110**. This negative electroactive particle having the multilayered coating including the first coating **120** and second coating **130** may be incorporated into a negative electrode. It should be noted that more than two layers of coatings may be applied or formed on the negative electroactive particle **100**.

In certain aspects, at least one of the first coating **120** or the second coating **130** may be an electrically conductive and ionically conductive layer that comprises a carbon-containing or carbonaceous material. In certain aspects, the electrically conductive and ionically conductive layer may comprise an amorphous carbon that generally lacks any crystalline structure or ordering. Amorphous carbon generally has superior mechanical properties, such as tensile strength, for withstanding the volumetric changes of the electroactive material. Further, the electrically conductive and ionically conductive layer may also comprise a graphitic carbon, which is crystalline and has ordering. As will be described further below, graphitic carbon exhibits good electrical conductivity. Generally, the graphitic carbon may have an sp2/sp3 ratio of bonds ranging from about 70:30 to about 100:1. In an example, the ratio of sp^2 carbon to sp^3 carbon in the carbon coating may be about 74 to about 26. Such an electrically conductive and ionically conductive layer can be formed in a pyrolysis process. In certain variations, the amorphous carbon may form a first layer within the first or second coatings **120**, **130** and the graphitic carbon may form a second layer within the first or second coatings **120**, **130**. However, there may not be a distinct compositional delineation between the layers, but rather a gradient region between the respective compositions that defines the coating. An outer region of the first or second coatings **120**, **130** may comprise graphitic carbon to provide good electrical conductivity, including good connection between adjacent electroactive particles.

Negative composite electrodes may comprise greater than or equal to about 50% to less than or equal to about 90% of an electroactive material (e.g., lithium-silicon-oxide material comprising lithium silicide and lithium silicate particles optionally having one or more coatings prepared in accordance with the present disclosure), optionally greater than or equal to about 5% to less than or equal to about 30% of an electrically conductive material, and a balance binder. Electrically conductive materials are well known in the art and include graphite, carbon black, carbon nanotubes, powdered nickel, conductive metal particles, conductive polymers, and combinations thereof. Useful binders include any of those described above. For example, useful binders may comprise a polymeric material and extractable plasticizer suitable for forming a bound porous composite, such as halogenated hydrocarbon polymers (such as poly(vinylidene chloride) and poly((dichloro-1,4-phenylene)ethylene), fluorinated urethanes, fluorinated epoxides, fluorinated acrylics, copolymers of halogenated hydrocarbon polymers, epoxides, ethylene propylene diamine termonomer (EPDM), ethylene propylene diamine termonomer (EPDM), polyvinylidene difluoride (PVDF), hexafluoropropylene (HFP), ethylene acrylic acid copolymer (EAA), ethylene vinyl acetate copolymer (EVA), EAA/EVA copolymers, PVDF/HFP copolymers, carboxy methyl cellulose (CMC), styrene butyl rubber (SBR), and mixtures thereof.

An electrode may be made by mixing the electrode active material, such as coated lithium-silicon oxide material containing powder or particles, into a slurry with a polymeric binder compound, a non-aqueous solvent, optionally a plasticizer, and optionally if necessary, electrically conductive particles. The slurry can be mixed or agitated, and then thinly applied to a substrate via a doctor blade. The substrate can be a removable substrate or alternatively a functional substrate, such as a current collector (such as a metallic grid or mesh layer) attached to one side of the electrode film. In one variation, heat or radiation can be applied to evaporate the solvent from the electrode film, leaving a solid residue. The electrode film may be further consolidated, where heat and pressure are applied to the film to sinter and calendar it. In other variations, the film may be air-dried at moderate temperature to form self-supporting films. If the substrate is removable, then it is removed from the electrode film that is then further laminated to a current collector. With either type of substrate, it may be necessary to extract or remove the remaining plasticizer prior to incorporation into the battery cell.

A battery may thus be assembled in a laminated cell structure, comprising an anode layer, a cathode layer, and electrolyte/separator between the anode and cathode layers. The anode and cathode layers each comprise a current collector. A negative anode current collector may be a copper collector foil, which may be in the form of an open mesh grid or a thin film. The current collector can be connected to an external current collector tab.

For example, in certain variations, an electrode membrane, such as an anode membrane, comprises the electrode active material (e.g., coated lithium-silicon-oxide containing particles) dispersed in a polymeric binder matrix over a current collector. The separator can then be positioned over the negative electrode element, which is covered with a positive electrode membrane comprising a composition of a finely divided lithium insertion compound in a polymeric binder matrix. A positive current collector, such as aluminum collector foil or grid completes the assembly. Tabs of the current collector elements form respective terminals for the battery. A protective bagging material covers the cell and prevents infiltration of air and moisture. Into this bag, a liquid electrolyte may be injected into the separator (and may be imbibed into the positive and/or negative electrodes) suitable for lithium ion transport. In certain aspects, the laminated battery is further hermetically sealed prior to use.

A surface coating (such as an oxide-based coating) applied to a negative electroactive material comprising a lithium-silicon-oxide composition in accordance with certain aspects of the present technology may be formed over the entire exposed surface and thus serve as an artificial solid electrolyte interface layer, which can protect the electrode from reaction with liquid electrolyte. In various aspects, the electroactive materials comprising lithium-silicon-oxide compositions may have a surface coating providing certain advantages, such as high cut voltage (e.g., cut-off potentials relative to a lithium metal reference potential) that desirably minimizes or avoids SEI formation. In certain aspects, a lithium-ion battery incorporating an inventive negative electroactive material having a lithium-silicon-oxide compositions electroactive material with optional coating(s) substantially maintains charge capacity (e.g., performs within a preselected range or other targeted high capacity use) for at least about 1,000 hours of battery operation, optionally greater than or equal to about 1,500 hours of battery operation, optionally greater than or equal to about 2,500 hours or longer of battery operation, and in certain aspects, optionally greater than or equal to about 5,000 hours or longer (active cycling).

In certain aspects, the lithium-ion battery incorporating an inventive negative electroactive/electrode material having a lithium-silicon-oxide composition electroactive material with optional coating(s) maintains charge capacity and thus is capable of operating within 20% of target charge capacity for a duration of greater than or equal to about 2 years (including storage at ambient conditions and active cycling time), optionally greater than or equal to about 3 years, optionally greater than or equal to about 4 years, optionally greater than or equal to about 5 years, optionally greater than or equal to about 6 years, optionally greater than or equal to about 7 years, optionally greater than or equal to about 8 years, optionally greater than or equal to about 9 years, and in certain aspects, optionally greater than or equal to about 10 years.

In other aspects, the lithium-ion battery incorporating an inventive electroactive material is capable of operating at less than or equal to about 30% change in a preselected target charge capacity (thus having a minimal charge capacity fade), optionally at less than or equal to about 20%, optionally at less than or equal to about 15%, optionally at less than or equal to about 10%, and in certain variations optionally at less than or equal to about 5% change in charge capacity for a duration of at least about 100 deep discharge cycles, optionally at least about 200 deep discharge cycles, optionally at least about 500 deep discharge cycles, optionally at least about 1,000 deep discharge cycles.

Stated in another way, in certain aspects, a lithium-ion battery or electrochemical cell incorporating the inventive negative electroactive material having a lithium-silicon-oxide electroactive material with optional coating(s) substantially maintains charge capacity and is capable of operation for at least about 1,000 deep discharge cycles, optionally greater than or equal to about 2,000 deep discharge cycles, optionally greater than or equal to about 3,000 deep discharge cycles, optionally greater than or equal to about 4,000 deep discharge cycles, and in certain variations, optionally greater than or equal to about 5,000 deep discharge cycles.

The present disclosure thus contemplates methods of forming the carbon-containing coatings and/or oxide-containing coatings on the negative electroactive materials comprising lithium-silicon-oxide materials. The carbon-containing coating can be formed in a pyrolysis process where a hydrocarbon is reduced to form a carbonaceous coating. The process for applying the oxide-based surface coating may be selected from a group consisting of atomic layer deposition (ALD), chemical vapor infiltration, chemical vapor deposition, physical vapor deposition, wet chemistry, and any combinations thereof. Indeed, in certain aspects, a deposition process may first comprise applying a carbon material to one or more surfaces of the electrode material by a first process, followed by applying a metal oxide material in a second process, or vice versa. Furthermore, in certain variations, a first coating may comprise an oxide-based coating, a second coating may comprise a carbon-based coating, and a third coating may comprise an oxide-based coating.

In certain aspects, the first and second processes may be in the same type of process or equipment, but the deposition or applying steps are carried out separately (e.g., sequentially) as described in U.S. Patent Publication No. 2021/0175491 entitled "Methods of Forming Prelithiated Silicon Alloy Electroactive Materials," the relevant portions of which are incorporated herein by reference. As will be described further herein, the first and second coating processes may be conducted in downstream reaction chambers in fluid communication with the centrifugal atomization reactor. In other aspects, the first and second processes may be entirely distinct from one another and/or further conducted separately after the formation of the negative electroactive lithium-silicon oxide material particles in the centrifugal atomization reactor.

The present disclosure thus contemplates methods of forming the carbon-containing coatings and/or oxide-containing coatings on the negative electroactive materials comprising lithium-silicon alloys. The carbon-containing coating can be formed in a pyrolysis process where a hydrocarbon is reduced to form a carbonaceous coating. The process for applying the oxide-based surface coating may be selected from a group consisting of atomic layer deposition (ALD), chemical vapor infiltration, chemical vapor deposition, physical vapor deposition, wet chemistry, and any combinations thereof. Indeed, in certain aspects, a deposition process may first comprise applying a carbon material to one or more surfaces of the electrode material by a first process, followed by applying a metal oxide material in a second process, or vice versa. Furthermore, in certain variations, a first coating may comprise an oxide-based coating, a second coating may comprise a carbon-based coating, and a third coating may comprise an oxide-based coating.

In certain aspects, the first and second processes may be in the same type of process or equipment, but the deposition or applying steps are carried out separately (e.g., sequentially). As will be described further herein, the first and second coating processes may be conducted in downstream reaction chambers in fluid communication with the centrifugal atomization reactor. In other aspects, the first and second processes may be entirely distinct from one another and/or further conducted separately after the formation of the negative electroactive lithium-silicon alloy particles in the centrifugal atomization reactor.

The foregoing description of the embodiments has been provided for purposes of illustration and description. It is not intended to be exhaustive or to limit the disclosure. Individual elements or features of a particular embodiment are generally not limited to that particular embodiment, but, where applicable, are interchangeable and can be used in a selected embodiment, even if not specifically shown or described. The same may also be varied in many ways. Such variations are not to be regarded as a departure from the disclosure, and all such modifications are intended to be included within the scope of the disclosure.

What is claimed is:

1. A method of making a negative electrode material for an electrochemical cell that cycles lithium ions, the method comprising:

centrifugally distributing a molten precursor comprising silicon, oxygen, and lithium by contacting the molten precursor with a rotating surface in a centrifugal atomizing reactor and solidifying the molten precursor to form a plurality of substantially round solid electroactive particles comprising a mixture of lithium silicide

(Li_ySi, where $0<y\leq 4.4$) and a lithium silicate (Li_4SiO_4) and having a D50 diameter of less than or equal to about 20 micrometers,

wherein a temperature in the centrifugal atomizing reactor is greater than or equal to 400° C. to less than or equal to about 800° C. during the centrifugally distributing.

2. The method of claim **1**, wherein the molten precursor is formed by melting a precursor comprising silicon (Si) and lithium oxide (Li_2O).

3. The method of claim **2**, wherein the precursor comprises a mole ratio of silicon (Si) to lithium oxide (Li_2O) of greater than or equal to about 1:2 to less than or equal to about 2:1.

4. The method of claim **2**, wherein the precursor further comprises silicon dioxide (SiO_2).

5. The method of claim **1**, wherein the lithium silicide is further represented by the formula $Li_{4.4x}Si$, where x is greater than 0 and less than or equal to about 0.85.

6. The method of claim **1**, wherein the plurality of substantially round solid electroactive particles comprise a coating selected from the group consisting of: carbon-containing coatings, oxide-containing coatings, and combinations thereof.

7. The method of claim **1**, wherein an environment in the centrifugal atomizing reactor has less than or equal to about 0.5% by weight of any oxygen-bearing species.

8. The method of claim **1**, wherein a flow rate of the centrifugal atomizing reactor is greater than or equal to 50 kg/hour to less than or equal to about 500 kg/hour.

9. The method of claim **1**, wherein the D50 diameter is greater than or equal to about 1 μm to less than or equal to about 10 μm.

10. The method of claim **1**, wherein the plurality of substantially round solid electroactive particles has a polydispersity index of less than or equal to about 1.2.

11. A method of making a negative electrode material for an electrochemical cell that cycles lithium ions, the method comprising:

centrifugally distributing a molten precursor by contacting the molten precursor with a rotating surface in a centrifugal atomizing reactor, wherein the molten precursor is formed from a mixture comprising silicon dioxide (SiO_2), lithium oxide (Li_2O), and silicon (Si); and

solidifying the molten precursor to form a plurality of substantially round solid electroactive particles comprising a mixture of lithium silicide (Li_ySi, where $0<y\leq 4.4$) and a lithium silicate (Li_4SiO_4) and having a D50 diameter of less than or equal to about 20 micrometers.

12. The method of claim **11**, wherein the mixture comprises a mole ratio of silicon (Si) to lithium oxide (Li_2O) of greater than or equal to about 1:2 to less than or equal to about 2:1.

13. The method of claim **11**, wherein the lithium silicide is further represented by the formula $Li_{4.4x}Si$, where x is greater than 0 and less than or equal to about 0.85.

14. The method of claim **11**, wherein a temperature in the centrifugal atomizing reactor is greater than or equal to 400° C. to less than or equal to about 800° C. during the centrifugally distributing.

15. The method of claim **11**, wherein a flow rate of the centrifugal atomizing reactor is greater than or equal to 50 kg/hour to less than or equal to about 500 kg/hour.

16. The method of claim **11**, wherein the D50 diameter is greater than or equal to about 1 μm to less than or equal to about 10 μm.

17. The method of claim **11**, wherein the plurality of substantially round solid electroactive particles has a polydispersity index of less than or equal to about 1.2.

18. A method of making a negative electrode material for an electrochemical cell that cycles lithium ions, the method comprising:

melting a precursor mixture comprising lithium oxide (Li_2O) and silicon (Si) to form a molten precursor;

centrifugally distributing the molten precursor by contacting the molten precursor with a rotating surface in a centrifugal atomizing reactor; and

solidifying the molten precursor to form a plurality of substantially round solid electroactive particles comprising lithium silicide (Li_ySi, where $0<y\leq 4.4$) and a lithium silicate (Li_4SiO_4) and having a D50 diameter of less than or equal to about 20 micrometers.

19. The method of claim **18**, wherein the precursor mixture further comprises silicon dioxide (SiO_2).

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